Copper Isotope Separation by Ion Exchange Electromigration and Copper Isotope Analysis by Thermo-Ionization Mass Spectrometry

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The separation coefficient of copper isotopes, ^{63}Cu and ^{65}Cu, in the electromigration process through cation exchange membrane was experimentally determined as 3.2×10^{-4}. The appropriate heating condition of low ionizing filament current for thermo-ionization mass spectrometry was developed and this method was applied to the copper isotope analysis in the present work.

Due to the high ionization potential of copper there have been difficulties in using the double-filament thermo- (or surface) ionization method in the mass spectrometric analysis of copper. Instead one has used ionization by electron bombardment [1] or thermo-ionization with the copper electro-plated on filaments [2].

In the present work a simple and convenient method of copper isotope analysis has been developed and successfully applied to copper samples taken from an exchange electromigration experiment.

Experimental

Electromigration

The cation exchange membrane Aciplex CK-1 (produced by Asahi Chemical Industry Co.) was used as the migration medium. The migration apparatus and processes were similar to those in the previous work on calcium isotope separation [3]. The major conditions of the experiment are summarized in Table 1. The migration was carried out in a break through manner. After the migration the front boundary part of the copper adsorption band was cut into narrow of 5 mm width and the copper in the sample segments was eluted with 2 M (mol/dm^3) HNO_3. The concentration of each sampled copper was determined with flame photometry at 324.7 nm.

Isotope Analysis

A mass spectrometer MAT-CH4 equipped with a thermo ionization ion source employing a double filament cartridge was used.

At first appropriate measuring conditions were established (see below). Based on these conditions, a protion of the copper sample (ca. 100 µg $Cu(NO_3)_2$) was placed on the vaporizing filament in a cartridge, brought into the ion source and measured concerning the copper isotopes.

Results and Discussion

In the previous work on calcium isotope analysis it was found that calcium was thermally ionized at two different conditions of the vaporizing filament current. This stimulated the interest in the heating conditions in the present case. Figure 1 demonstrates that the ^{63}Cu ion beam first appeared at the ionizing filament (IF) current 1 A (current increase rate approximately 50 mA/min), reached a maximum intensity at 2 A and then decreased with increasing current. Meanwhile the vaporizing filament (VF) current was zero. However the copper ion beam was again produced at the IF current 5.5 A and the VF current around 3 A.

Since the ionization potential of copper is very high, as high as 7.7 eV, the high heating condition is reasonable for the normal process of thermal ionization. The low heating condition, however, was unexpected. In the previous work we have found that calcium is thermally ionized at two different heating conditions of the VF; the heating current of the IF is commonly 5.5 A (with W tape or 4 A with Re tape) [3]. For the calcium ionization we have proposed that calcium iodide is evaporated at low temperature and ionized on the strongly heated surface of the IF, while in the high temperature region CaI_2 is converted to CaO and vaporized only at high temperature of the VF.

Table 1. Conditions of the copper electromigration experiment using a cation exchange membrane.

Anode solution	0.5 M $Cu(NO_3)$
Migration length	93.5 cm
Current density	125 mA/cm^2
Applied voltage	170 ~ 820 V
Temperature	25 °C

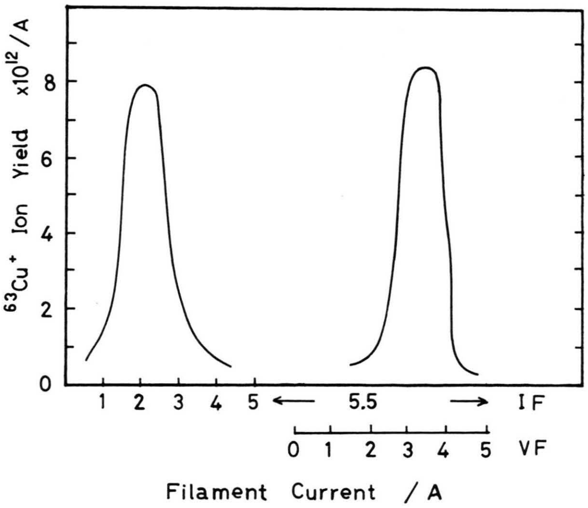

Fig. 1. Thermo-ionization of copper in a mass spectrometer. IF: Ionizing filament (Re). VF: Vaporizing filament (Re).

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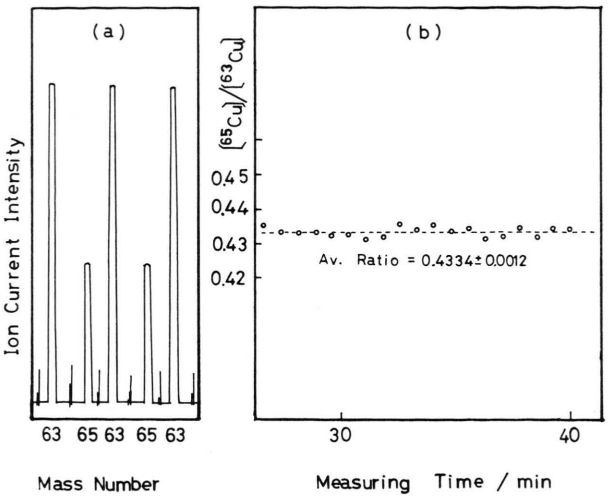

Fig. 2. Recorded mass spectra of copper isotopes (a) and the measured isotopic ratio (b). Measuring conditions: Ionizing filament current 2 A and sensitivity 0.1 V.

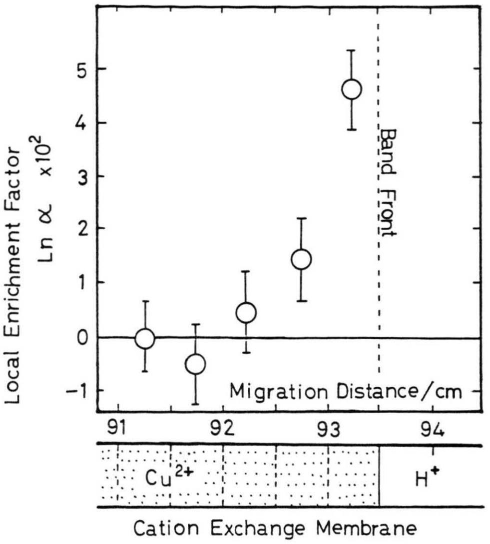

Fig. 3. Local enrichment factors of copper isotopes in the front of migration band.

The surface of the IF used for the copper ionization tests was examined and found quite normal (smooth and bright) when taken out after the high heating at 5.5 A, while the surface was covered with a very thin layer of red-brown copper compounds when taken out after the low heating at 2 A. This suggests that copper nitrate molecules evaporate from the VF, deposit on the IF and are decomposed there to oxide species. At this low heating condition, many peaks of hydrocarbones were observed in the mass range 100−300, corresponding to the fragments of ion exchange resin involved in the copper samples. It seems that at the low heating condition the IF merely serves to heat by radiation the surface of the salt on the VF, this surface emitting not only nitrate molecules but also copper ions.

Figure 2 shows the copper mass spectra and the copper isotope ratios, recorded in the isotope analysis with the low heating condition. The isotope analysis tested with the high heating condition was unsuccessful due to an instability in the copper ion formation.

The results of the isotope analysis for the samples of exchange electromigration are plotted in Figure 3. The local enrichment factor α is defined as

$$\alpha = [^{63}\mathrm{Cu}/^{65}\mathrm{Cu}]_{\mathrm{sample}}/[^{63}\mathrm{Cu}/^{65}\mathrm{Cu}]_{\mathrm{original}}\,. \qquad (1)$$

Figure 3 indicates that ^{63}Cu is enriched at the front boundary. The separation coefficient ε of the present system was calculated in the same way as mentioned in the previous work [3]. Thus we obtained the value $\varepsilon = 3.2 \times 10^{-4}$ (the error was estimated to be 10% of ε). Deviding with the mass difference, $\Delta M = 2$ amu, we obtained the separation coefficient per unit mass difference, $\varepsilon/\Delta M$, as 1.6×10^{-4}. This value is slightly smaller than the value of calcium, 1.85×10^{-4} (at 25 °C), but much larger than the one for uranium, 2.7×10^{-5} [4]. More detailed considerations will be made in the next work, specifically on the correlation between the separation coefficients and the electrochemical properties.

[1] E. J. Spitzer, and J. R. Sites, Isotopic Mass Spectrometry of the Elements, ORNL-3528, p. 21, US AEC, Washington D.C.
[2] W. R. Shields, T. J. Murphy, and E. L. Garner, J. Res. Nat. Bur. Stand. **68a**, 589 (1964).
[3] Y. Fujii, J. Hoshi, H. Iwamoto, M. Okamoto, and H. Kakihana, Z. Naturforsch. **40a**, 843 (1985).
[4] Y. Fujii, H. Kakihana, M. Okamoto, T. Oi, and Y. Sakuma, Isotopenpraxis **15**, 203 (1979).

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